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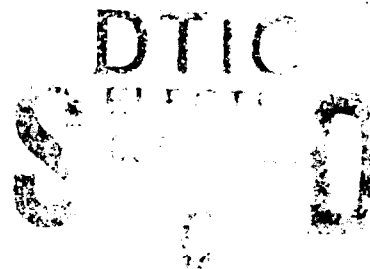


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Electrochemical and Scanning Tunneling Microscopic Study  
of Dealloying of  $\text{Cu}_3\text{Au}$

by

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# Electrochemical and Scanning Tunneling Microscopic Study of Dealloying of $\text{Cu}_3\text{Au}$

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## ABSTRACT

Dealloying of  $\text{Cu}_3\text{Au}$  has been examined by in-situ STM and several electrochemical methods. Three different regimes of behavior were noted. At low overpotentials, clustering of gold atoms occurs near sites of copper dissolution. This is essentially a two-dimensional process. The formation and smoothing of these clusters by capillary action, monitored in real time, demonstrated the highly mobile nature of the surface species. At higher potentials, the electrode is largely passivated by the enrichment of gold. However, there exist small localized regions of three-dimensional roughness which may be correlated to extended dealloying catalyzed by bulk solid-state defects. When the potential is increased above the critical potential ( $E_C$ ), global surface roughening occurs. Correlating STM with chronoamperometric and chronopotentiometric results demonstrates that this transition occurs by nucleation and growth. Selective dissolution of copper depends on the exposure of fresh sites by the migration of passivating gold atoms. Adsorption can strongly influence this transport process, as manifest by changes in  $E_C$ . In comparison to sulfate media, chloride caused a decrease in  $E_C$ , while derivatization of  $\text{Cu}_3\text{Au}$  with an alkyl-thiol produced an increase in  $E_C$ . These shifts are consistent with the enhancement and inhibition of gold surface diffusion by the respective adsorbates.

Dealloying is a phenomenon of great importance in general corrosion (1, 2), stress corrosion cracking (2, 3), and catalysis (4). In the case of a binary alloy A-B, such as Cu-Au, dealloying entails the selective dissolution of the less-noble element A, in this case, copper. A schematic of a typical potentiostatic polarization curve is given in Figure 1. The curve exhibits a domain of very low potential-independent current followed by a region of rapidly increasing current. The potential defining the transition between these regimes is known as the critical potential,  $E_C$ .  $E_C$  is a strong function of alloy composition (1, 2). At potentials below  $E_C$ , dissolution of the active species, A, leads to an enrichment of the noble species B, in this case, gold, which suppresses the further dissolution of A. It is unclear if this blocking layer is pure B, or a B-enriched alloy. The critical potential is associated with the breakdown of this passivating overlayer and the onset of massive dealloying. At potentials greater than  $E_C$ , gross surface roughening occurs and the near-surface of the alloy evolves into a fine, porous, noble-metal enriched network. This process has been described as a cellular phase transformation (4). It has been suggested that the critical potential,  $E_C$ , defines the transition from a stable planar surface to a highly ramified interface (2).

A variety of mechanisms have been proposed to explain the breakdown phenomenon that leads to massive dealloying. Modern discussions have largely concentrated on the relative importance of volume diffusion versus surface transport processes (1). Pickering and Wagner (5) suggested that the rate of dealloying is controlled by solid-state diffusion of the less-noble metal via divacancies. Prior to this, Wagner (6) demonstrated that if volume diffusion controls the rate of dealloying, then geometrical instabilities will develop along the planar interface which will grow rapidly with time. This could account for the sponge-like morphology of the dealloyed layer. The critical

potential was ascribed to a potential-dependent concentration of divacancies (2). The large increase in defect density would occur at high overpotentials where oxidation from highly coordinated surface sites becomes possible. This mechanism depends on the blocking layer being B-enriched as opposed to a pure B overlayer. An alternative dealloying mechanism based on surface diffusion was proposed by Gerischer et al. (7), where the surface mobility of the more noble element governs the rate of selective dissolution. The critical potential was rationalized by a potential-dependent surface mobility. Selective dissolution proceeds via surface migration of B exposing new A sites to solution. Simultaneously, B atoms aggregate to form crystallites. Transmission electron microscopy (TEM) studies of Au-Ag alloys provide strong support for this mechanism (8). The high surface mobility was attributed to partial ionization and solvation (i.e., incipient oxidation) of gold. Forty et al. (9) developed a quantitative treatment to describe the pitting or tunnelling attack observed during massive dealloying. Similarly, Pryor et al. (10) portrayed dealloying as a short range process involving the collapse and recrystallization of B following the removal of A atoms. More recently, a percolation formalism (11), invoking surface diffusion, has been utilized to address this problem. Many of the morphological features observed by ex-situ TEM and SEM studies, e.g., clustering, smoothing, and local penetration phenomena, were favorably simulated.

To probe the mechanism of dealloying, Kaesche et al. (12, 13) used TEM and optical microscopy to examine the evolution of electrode morphology of a diverse series of alloys. Two limiting forms of behavior were revealed. Dealloying of "high-melting point" materials, e.g., Cu-Pd and Cu-Au, occurred by nucleation and growth of microtunnels, while dissolution of "low-melting point" alloys, e.g., SnIn, produced a homogeneous non-porous overlayer which was associated with the volume diffusion mechanism. Selective dissolution of

ε-brass exhibited both morphologies and was considered to represent an intermediate case between "high- and low-melting point" materials. Thus, the dealloying mechanism appears to correlate to the "melting-point" of the alloy, presumably by correspondence with the magnitude of the diffusion coefficient.

In spite of this growing body of knowledge, there is currently no model that successfully describes the relationship between alloy composition and  $E_C$ . Information on the precise composition and morphology of the B-enriched blocking layer would be useful toward resolving the nature of the breakdown process associated with  $E_C$ .

Part of the difficulty associated with understanding dealloying phenomena has been the lack of appropriate tools for examining the evolving interface. *In-situ* scanning tunneling microscopy (STM), with its attendant high spatial resolution and real-time capability, offers a means by which such electrochemical processes may be studied. A recent review of this technique is available (14). In this report, *in-situ* STM is utilized to address the nature of the critical potential associated with dealloying of  $Cu_3Au$ .

The Cu-Au system was investigated because gold dissolution does not occur at the potentials associated with dealloying (5). Consequently, the measured current can be attributed solely to the dissolution of copper (5, 15). Furthermore, the electrochemistry of the constituent elements and the metallurgy of the copper-gold system are well understood. At temperatures above 410 °C, Cu-Au alloys form a f.c.c. solid solution over the entire concentration range. At lower temperatures, however, a variety of ordered intermetallic structures are possible. Thus, by appropriate heat treatment,  $Cu_3Au$  provides an additional opportunity to investigate the effects of ordering on electrochemical behavior. Currently, there are conflicting results concerning this matter (15-17).